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THE ROLE OF PROPYLENE IN THE PARTIAL OXIDATION OF PROPANE

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ABSTRACT

The partial oxidation of propane and of mixtures of propane and propylene was studied in order to elucidate the role of propylene in the mechanism of propane oxidation. Propylene itself may be formed in substantial amounts in the oxidation of propane and it is also known to be an inhibitor in many types of free radical reactions. Particular attention was also directed to the mechanism of formation and destruction of hydrogen peroxide in the over all reaction, and the results are of interest in evaluating the industrial potential of a hydrocarbon oxidation process for the manufacture of hydrogen peroxide.

The experimental apparatus was a tubular borosilicate glass (Pyrex) flow reactor, preceded by separate hydrocarbon (propane and propylene) and oxygen preheaters, and followed by a tubular surface condenser cooled with circulating ice water. The range of experimental variables studied was as follows: reaction temperatures of 375, 425, and 475°C; propane-to-oxygen mole ratio of 5.5 to 1; inlet propylene concentrations of 0, 5, and 15 mole per cent; and residence times of 0.7 to 12 seconds.

At the lowest temperature, 375°C, very little ethylene and methane but considerable amounts of propylene and oxygenated organic compounds were formed per mole of propane reacted. At 425°C, the yield of oxygenated organic compounds decreased while the yield of propylene and hydrogen peroxide isolated per mole of propane reacted reached a maximum. At 475°C, only small amounts of oxygenated organic compounds were found but some ethylene and methane were detected in the products.

Propylene, added as a diluent, decreased the induction period of the oxidation, but had little effect on the subsequent rate of oxidation. Increased amounts of the oxygenated organic compounds were found in the products per mole of oxygen reacted as the concentration of diluent propylene was increased but at the same time the yield of hydrogen peroxide per mole of oxygen reacted

decreased. No significant effect of propylene addition was noted on the amount of hydrogen peroxide plus water isolated per mole of oxygen reacted. The reaction rate at 425°C was found to be much slower than at either 375 or 475°C.

The results are interpreted in terms of a reaction mechanism. It appears probable that the decrease noted in the length of the induction period when diluent propylene was added is caused by oxygen attacking propylene to form allyl and perhydroxyl radicals at a higher rate than it attacks propane. The perhydroxyl radical and some of the allyl radicals formed in the reaction are postulated to react then with propane to form the propyl radical, this two-step process being more rapid than the single-step reaction of oxygen with propane. Propylene decreases the amount of aldehydes decomposing by free-radical attack by reacting preferentially with the free radicals to form the relatively inactive allyl radical. This sequence leads to higher yields of aldehydes in the products.

It was concluded that substantially larger quantities of hydrogen peroxide were formed in the reaction than were actually isolated. The hydrogen peroxide yield was found to vary with the type and condition of the reactor surface. The highest yields were found in new, clean borosilicate glass (Pyrex). Propylene addition decreased the yield of hydrogen peroxide per mole of oxygen reacted, but the total yield of water plus hydrogen peroxide was not greatly changed. This indicates that propylene was causing some decomposition of hydrogen peroxide to water, possibly by being adsorbed on the reactor wall and rendering it more active toward peroxide destruction.

The allyl radical produced from propylene by reaction with oxygen or a free radical is resonance stabilized and is considered relatively inert compared to the propyl radicals formed from propane. Attempts to oxidize pure propylene showed that under comparable experimental conditions, essentially no reaction occurred at residence times in which propane-oxygen mixtures were almost completely reacted.

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The partial oxidation of propane and of mixtures of propane and propylene was studied in order to elucidate the role of propylene in the mechanism of propane oxidation and to aid in the evaluation of the industrial potentialities of such an oxidation process for producing hydrogen peroxide. In these experiments substantial quantities of the following intermediate products of the oxidation were isolated: formaldehyde, acetaldehyde, methanol, hydrogen peroxide, carbon monoxide, and the olefins propylene and ethylene. The theoretical significance of such studies proceeds from the fact that propylene is itself formed in the reaction and it has been found in general to inhibit free radical reactions. In practical operations, the propane feed gas for an industrial plant, whether obtained from the petroleum refinery or from recycling the unreacted propane in a partial oxidation process, may contain some propylene. The knowledge of how this diluent affects the yields of hydrogen peroxide and other products would indicate whether the propylene must first be separated from the propane feed gas.

The literature indicates that the oxidation of propane has been more extensively investigated than that of any other hydrocarbon. A recent report (17) gives references to the previous work. The rate and products of the oxidation are greatly influenced by the reaction temperature. At pressures of 1 to 2 atmospheres and with a high ratio of propane to oxygen, the important effects of temperature may be summarized as follows (16):

1. At temperatures below 375°C, the products of the reaction are mainly formaldehyde, acetaldehyde, and methanol although some propylene is also formed.

2. As the temperature is raised above 375°C, a range is reached in which the rate of oxidation decreases with increasing temperature. The exact range of this negative temperature coefficient can vary with the partial pressure of reactants and surface conditions but is usually observed between 400-425°C. With further increase in temperature the rate passes through a minimum and then increases.

3. In the range of the negative temperature coefficient, as the temperature is raised the proportion of oxygenated products decreases and that of the olefins increases.

4. As the reaction rate increases after passing through the minimum, the proportion of reacted propane going to oxygenated organic products continues to decrease and the proportion going to olefins, increases. Ethylene production increases very rapidly, and above about 500-550°C, the reaction becomes essentially an oxygen-sensitized cracking of propane.

Hydrogen peroxide is reported as a product at temperatures between 300-500°C, but the quantities isolated depend to a great extent on the type of reactor surface used in the experiments as well as the temperature and reactant ratios. When soft glass or salt coated glass reactors are used, very little hydrogen peroxide is found but when Pyrex or silica glass reactors are substituted, the yields of hydrogen peroxide increase. The amounts of hydrogen peroxide appear to increase with temperature, but often the increased decomposition rate of this species at the higher temperatures leads to lower overall yields.

The effect of propylene addition was noted by two previous investigators with conflicting results; Chernyak and Shtern (5) reported that the addition of propylene had no effect on either the rate or the product distribution; the propylene which was added reportedly passed through unchanged. Harris and Egerton (8) found that propylene addition decreased the induction period in propane oxidation but did not change the final amount of propylene isolated. Neither attempted any explanation of their results.

EXPERIMENTAL

The experimental apparatus consisted of a tubular Pyrex flow reactor, 1 inch i.d. and 3 feet long, preceded by separate, electrically heated hydrocarbon (propane and propylene) and oxygen preheaters and followed by a tubular surface condenser cooled with circulating ice-water. The arrangement is shown on Figure 1. Since back-mixing would confuse kinetic interpretation of results, a long cylindrical reactor shape was chosen so as to make the flow

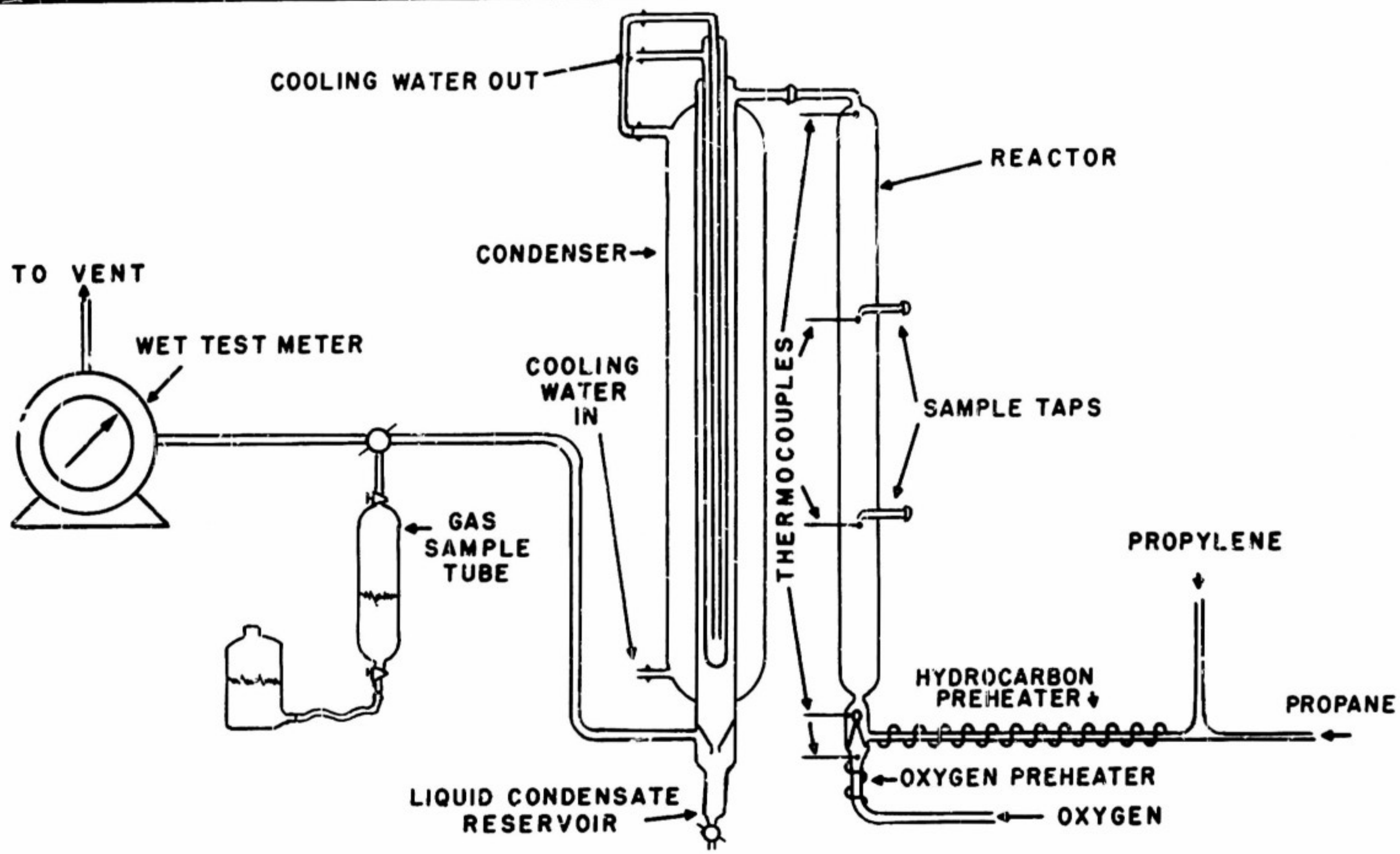

FIGURE I

APPARATUS USED IN EXPERIMENTS

characteristics of the reacting gases approach slug flow as nearly as possible. Propylene and propane of 99% purity and oxygen of 99.5% purity were used as the reactants. The propylene was metered separately and added to the propane stream just prior to the hydrocarbon preheater. The residence time was varied by changing the inlet flow rates; this in turn controlled the amount of reaction occuring. The first 24 inches of the reactor was maintained isothermal by insulation and electrical heaters. Either electrical heating or cooling by forced air convection could be externally applied to the last 12 inches of the reactor, the cooling being necessary to maintain isothermal conditions in runs in which a large amount of reaction took place. Temperatures were measured of the hydrocarbon and oxygen gases before they were mixed at the reactor inlet and of the reacting gases at every 12 inches along the reactor.

In each run, the oxidation was allowed to reach steady state, after which liquid and gas flow rates were measured and samples of both streams collected. The gas samples were analyzed volumetrically by selective chemical absorption for carbon dioxide, acetylene, propylene, ethylene, oxygen, and carbon monoxide (2); hydrogen was selectively oxidized by copper oxide; and methane was determined by infrared absorption. Propane was determined by difference. Acetylene was never detected in the exit gas by this chemical absorption technique except in a few runs where pure propylene was oxidized. Previous work (17) has shown that small amounts of ethane are also present in the product gas but essentially no olefins higher than propylene nor saturated hydrocarbons higher than propane are found. This latter result suggests that polymerization reactions of hydrocarbon radicals here are negligible.

The liquid condensate was analyzed as follows (17(a)): total peroxide was determined iodimetrically using 56% hydriodic acid in glacial acetic acid solvent; total aldehyde was determined by measuring the amount of acid liberated using hydroxylamine hydrochloride; formaldehyde was determined colorimetrically with acidified Schiff's reagent; methanol was determined colorimetrically with ceric ammonium nitrate after separation of the methanol from the aldehydes and peroxides. Acetaldehyde was calculated as the difference between the total aldehyde and formaldehyde.

The intensity of the purple color developed when Schiff's reagent reacts with formaldehyde is decreased when the formaldehyde solution also contains hydrogen peroxide. The hydrogen peroxide reacts with the formaldehyde to form organic peroxides which are apparently incompletely reconverted to formaldehyde in the analytical procedure. Correction factors were therefore established by determining the effect on the reported value of (1) the time that the formaldehyde and hydrogen peroxide were in contact with one another before analysis, (2) the temperature, and (3) the initial concentration of formaldehyde and hydrogen peroxide. By this means it was possible to determine formaldehyde concentrations to within ± 10% of the true value.

A check on the overall accuracy was obtained by calculating material balances from the analytical results for the gas and liquid samples, combined with the flow rate measurements. The quantity of the liquid condensate, as measured by direct weighing of a sample taken over a known time interval, was corrected for the amounts of the liquid components left uncondensed in the gas phase. The gas stream left the condenser at a temperature between 5-10°C and presumably was in equilibrium with the liquid condensate. The results of some experiments by Cooper (6) were used to calculate the equilibrium partial pressures of the liquid components in the exit gas stream and these data, combined with a knowledge of the total gas flow from the condenser, made it possible to calculate the amount of the various liquid components carried out of the condenser by the exit gas. This correction affects particularly the amount of methanol reported since it is quite volatile in dilute aqueous solutions. Studies were made at three different temperatures; 375°C, representative of the so-called low-temperature oxidation region; 425°C, which is in the temperature region where the rate of reaction has a negative temperature coefficient; and 475°C, representative of the high-temperature region.

In all studies the molar ratio of propane to oxygen was kept constant at 5.5 to 1. Each series of experiments consisted of three runs: in the first, propane and oxygen were reacted with no propylene added. In the second, a concentration of propylene equal to 5% of the total entering gases was used; in the third 15% propylene was added. All three runs were carried out at the same contact time, achieved by reducing the propane and oxygen flow rates as propylene was added. The residence times reported were calculated by dividing the reactor volume by the entering gas volumetric flow rate, corrected to the temperature prevailing in the reactor. This method of calculating residence times, of course, gives only an approximation to the "true" contact time because there is an increase in the number of moles during the reaction, and slug flow is not completely achieved. By varying the residence time in successive studies, the progress of the reaction was followed from the early stages up to the point where essentially all of the inlet oxygen had reacted. A total of 48 runs were made.

RESULTS

The experimental results are presented in tabular form in Tables 1, 2, and 3. The moles of reactants entering and products leaving the reactor are shown in Table 1 on a basis of one hour of operation and in Table 2 on a basis of 100 moles of total inlet gases. Table 2 also lists the percent of inlet oxygen reacted and the results of material balances on carbon, hydrogen, and oxygen. Table 3 presents the product yield per mole of oxygen reacted.

The general effect of the variables of reaction temperature, inlet propylene concentration, and extent of reaction on the product distribution and rate of reaction may be briefly summarized as follows:

Reaction Temperature

The effect of temperature was similar to that noted by previous investigators. At the low temperature, 375°C, the products consisted largely of oxygenated organic species in addition to some propylene. At 425°C, in the negative reaction rate zone, the quantities of oxygenated organic compounds decreased and some ethylene and methane were found. The yield of propylene and

TABLE 1

TABLE OF EXPERIMENTAL DATA

Run No.	Temperature °C	Flow Rates Gm Moles/Hr. C_3H_8	O_2	C_3H_6	Exhaust Gas	Gms/Hr. Condensate	Exhaust Gas Composition (Dry Basis) CO_2	C_2H_4	C_3H_6	C_2H_6	O_2	CO	H_2	CH_4	C_3H_8	Condensate Composition Weight Percent H_2O	H_2O_2	CH_3CHO	$HCHO$	CH_3OH
4A	375	4.40	0.80	--	4.41	30.2	0.6	--	5.4	1.2	0.4	5.6	1.4	--	85.3*	36.7	9.9	6.3	18.8	28.2
4B	375	4.18	0.76	0.26	4.47	29.1	0.0	--	8.9	1.1	0.7	5.3	--	--	84.0**	34.7	9.4	2.7	20.6	32.5
4C	375	3.74	0.68	0.78	4.57	25.4	0.4	--	17.3	0.7	0.2	5.2	--	1.1	79.3***	34.9	9.1	8.3	21.3	26.4
5A	375	6.60	1.20	--	6.81	33.6	0.1	--	4.5	0.6	6.2	2.5	2.2	1.9	83.0	36.3	14.3	14.3	14.3	20.8
5B	375	6.25	1.14	0.39	6.64	35.5	0.2	--	9.1	1.4	3.9	3.3	0.8	0.8	80.5	31.6	16.4	13.5	16.1	22.4
5C	375	5.60	1.02	1.16	6.72	34.5	0.5	--	17.5	1.0	0.9	4.1	0.3	1.1	74.4	32.4	16.3	15.3	16.5	19.4
6A	375	8.74	1.61	--	9.85	24.5	0.1	--	2.8	0.7	10.6	0.9	0.9	1.4	82.6	35.6	18.7	15.9	13.6	16.1
6B	375	8.31	1.53	0.52	9.66	25.9	0.0	--	8.4	0.4	8.9	1.4	1.0	0.0	79.7	31.6	17.7	15.8	13.9	20.9
6C	375	7.30	1.34	1.48	9.40	34.4	0.2	--	17.3	1.5	5.9	1.6	1.2	0.9	71.3	28.8	17.6	23.0	11.3	19.3
7A	375	10.5	1.91	--	12.4	13.6	0.0	--	1.4	0.1	13.5	0.1	0.9	1.3	82.7	31.3	15.5	7.4	20.6	25.2
7B	375	9.99	1.81	0.62	12.0	25.6	0.2	--	6.5	0.2	11.0	0.6	1.[illegible]	--	80.3*	34.8	12.9	5.5	24.6	22.1
7C	375	8.91	1.61	1.85	11.4	33.7	0.3	--	16.8	0.6	6.8	1.4	1.0	0.5	72.6	31.7	14.9	8.6	21.4	23.4
8A	375	4.50	0.81	--	5.21	3.78	0.1	0.0	1.9	0.3	14.8	0.4	0.6	0.6	81.3	37.0	12.7	9.0	17.5	23.8
8B	375	4.28	0.78	0.27	5.07	10.0	0.1	0.0	6.7	0.2	12.0	1.6	0.2	0.0	79.2	31.9	9.2	14.0	23.0	22.0
8C	375	3.82	0.69	0.79	5.03	8.54	0.2	--	16.5	0.4	10.1	0.8	0.9	0.4	70.7	32.6	11.7	4.1	27.0	24.6
9A	475	6.68	1.20	--	7.76	35.3	0.0	--	13.7	10.8	0.4	3.9	4.1	7.4	59.7	82.2	3.1	2.1	5.7	6.8
9B	475	6.38	1.14	0.40	7.62	34.4	0.3	--	15.9	8.7	0.2	4.3	1.3	6.1	63.2	81.2	1.7	0.8	7.0	9.3
9C	475	5.67	1.03	1.19	7.36	28.9	0.4	--	19.2	6.7	1.9	3.6	1.0	5.0	62.2	77.1	2.8	1.7	7.6	10.7
10A	475	9.38	1.67	--	10.7	55.[illegible]	[illegible].2	0.0	13.4	9.2	0.6	3.3	2.0	7.0	64.3	78.6	3.8	5.3	3.6	8.7
10B	475	8.85	1.59	0.55	10.7	48.4	0.0	--	16.2	10.2	0.5	3.9	3.0	7.1	59.1	81.0	1.5	1.7	6.8	8.9
10C	475	7.75	1.40	1.61	10.32	39.1	0.0	--	21.2	8.2	0.3	4.4	1.3	7.2	57.4	77.7	2.8	1.7	8.2	5.6
11A	475	9.61	1.74	--	10.7	24.8	0.0	--	5.5	1.0	10.5	0.9	1.1	0.7	80.3	45.2	32.7	10.5	4.8	6.7
11B	475	9.22	1.67	0.57	10.65	25.5	0.0	--	10.0	1.1	9.3	0.8	0.6	0.5	77.[illegible]	49.1	27.7	9.4	7.0	6.7
11C	475	8.12	1.47	1.69	10.3	30.1	0.0	--	18.8	1.5	6.1	1.1	0.6	0.6	71.1	49.5	22.6	13.6	6.6	7.6
12A	475	6.81	1.23	--	7.36	28.5	0.0	--	8.8	2.0	6.8	1.3	1.5	1.1	78.5	58.6	20.3	7.7	5.3	8.1
12B	475	6.47	1.14	0.[illegible]	7.24	32.6	0.2	--	14.0	3.6	3.1	2.4	1.5	2.6	72.6	58.0	18.7	9.5	5.2	8.6
12C	475	5.80	1.05	1.21	7.13	33.8	0.2	--	21.2	3.8	1.6	3.3	0.8	2.6	66.5	57.4	16.0	11.5	6.8	8.3
13A	475	6.59	1.22	--	7.48	18.9	0.0	--	6.7	1.3	10.0	0.7	0.6	2.7	78.0	53.3	25.0	8.4	5.8	7.4
13B	475	6.49	1.15	0.41	8.26	31.0	0.2	--	15.3	11.7	0.5	4.8	2.4	8.5	56.6	87.2	1.0	2.4	3.2	6.1
13C	475	5.74	1.03	1.19	8.39	27.7	0.4	--	21.1	10.7	0.6	4.8	2.0	7.9	53.0	57.4	16.0	11.5	6.8	8.3
14A	475	10.75	1.93	--	12.5	13.5	0.0	--	3.0	0.3	12.7	0.4	0.9	0.7	82.0	39.6	36.1	11.8	5.5	6.9
14B	475	10.4	1.83	0.65	12.5	14.6	0.0	--	7.6	0.6	12.1	0.2	1.2	0.4	77.9	47.0	30.1	10.3	6.2	6.4
14C	475	9.00	1.62	1.88	12.1	13.0	0.0	--	16.7	0.4	10.0	0.3	1.0	0.2	71.4	43.2	26.5	15.4	7.4	7.4
15A	425	6.27	1.16	--	7.20	4.29	0.0	--	2.0	0.1	14.8	0.0	0.7	--	82.4*	48.2	42.9	3.5	1.6	4.0
15B	425	5.86	1.07	0.37	6.96	8.43	0.0	--	7.0	0.1	12.6	0.3	0.7	0.2	79.1	46.5	35.3	13.0	1.5	3.6
15C	425	5.25	0.95	1.10	6.76	12.4	0.0	--	17.5	0.6	7.8	0.9	0.9	--	72.3*	49.0	35.6	12.1	2.3	1.0
16A	425	4.09	0.75	--	4.63	9.49	0.0	--	4.6	0.4	11.3	0.6	0.7	--	82.4*	42.4	34.0	8.8	9.8	4.8
16B	425	3.92	0.71	0.24	4.48	12.7	0.1	--	9.4	0.7	8.8	0.7	0.5	0.8	79.0	43.0	29.5	5.9	15.0	6.6
16C	425	3.51	0.63	0.73	4.40	19.9	0.2	--	19.5	1.5	1.7	2.5	0.8	0.3	73.5	47.0	22.7	7.1	14.6	8.6
17A	425	3.10	0.56	--	3.44	11.6	0.0	--	7.2	1.0	7.4	1.1	1.3	0.5	81.5	40.6	33.2	14.7	6.0	6.1
17B	425	2.94	0.53	0.19	3.32	15.9	0.0	--	12.2	1.6	2.8	2.2	0.5	--	81.7*	44.5	27.7	15.0	5.8	6.9
17C	425	2.68	0.46	0.55	3.36	16.1	0.4	0.0	19.9	2.3	0.6	3.9	1.1	1.6	70.2	52.6	18.8	11.2	8.7	8.7
18A	425	2.15	0.37	--	2.38	12.2	0.4	--	11.6	4.4	0.9	3.3	3.1	4.6	71.7	52.4	22.0	13.9	4.9	6.8
18B	425	2.32	0.42	0.14	2.66	13.9	0.3	--	13.6	2.9	0.5	3.8	1.2	--	77.7*	60.3	15.6	12.2	3.9	7.9
18C	425	10.4	1.89	2.23	14.5	10.5	0.0	--	15.5	0.2	11.4	0.2	0.7	0.1	71.9	44.2	27.6	16.2	7.1	4.9
19A	425	2.48	0.45	--	2.68	13.7	0.1	--	10.6	1.8	2.1	2.4	2.0	1.9	79.1	52.9	26.1	3.2	11.7	6.1
19B	425	4.65	0.84	0.29	5.55	9.04	0.1	--	7.9	0.5	11.0	0.4	0.7	0.1	79.3	42.8	32.0	4.0	15.5	5.8
19C	425	4.15	0.76	0.87	5.30	18.2	0.2	--	19.1	0.8	5.1	1.6	1.1	0.5	71.6	41.6	24.8	9.9	15.9	7.7

* Includes methane ** Includes methane and hydrogen *** Includes hydrogen

TABLE 2

TABLE OF RESULTS

Run No.	Temperature °C	Mole Ratio C_2H_6/O_2	Mole Ratio C_2H_6/C_2H_4	Residence Time Secs.	% Inlet Oxygen Reacted	MOLES OF PRODUCT PER 100 MOLES OF ENTERING GAS														MATERIAL BALANCE (Input−Output)/Input		
						CO_2	C_2H_2	C_2H_4	C_2H[illegible]	O_2	CO	H_2	CH_4	C_2H_6	H_2O	H_2O_2	CH_3CHO	HCHO	CH_3OH	%C	%H	%O
4A	375	5.5	—	5.9	97	0.5	—	4.4	1.0	0.3	4.8	1.2	—	72.9*	11.9	1.7	0.83	3.6	5.1	+2.3	+0.8	-3.5
4B	375	5.5	16	5.9	96	0.0	—	7.5	1.0	0.6	4.5	—	—	72.1**	10.8	1.6	0.35	3.8	5.7	0.0	-1.7	-1.3
4C	375	5.5	4.8	5.9	95	0.4	—	15.2	0.6	0.2	4.5	--	1.0	65.2***	9.5	1.3	0.92	3.5	4.0	+0.2	-0.7	0.0
5A	375	5.5	--	3.9	66	0.1	—	3.9	0.6	5.4	2.2	1.0	1.7	72.6	8.7	1.8	1.4	2.0	2.8	+5.2	+3.1	-2.1
5B	375	5.5	16	3.9	78	0.2	—	9.7	1.2	3.3	2.0	0.7	0.7	68.6	7.9	2.2	1.4	2.4	3.2	+4.4	-3.3	-0.9
5C	375	5.5	4.8	3.9	94	0.4	--	15.1	0.9	0.8	3.5	0.3	1.0	64.2	8.0	2.1	1.5	2.4	2.7	+2.8	+1.5	+5.0
6A	375	5.4	--	2.9	36	0.1	—	2.7	0.7	10.0	0.9	0.9	1.4	78.5	4.7	1.3	0.85	1.1	1.2	+0.7	-0.2	-1.5
6B	375	5.6	16	2.9	42	0.0	—	7.8	0.6	8.3	1.4	1.0	0.0	74.3	4.4	1.3	0.9	1.2	1.6	+0.8	+0.6	+3.3
6C	375	5.5	4.9	3.0	55	0.2	—	16.0	1.4	5.5	1.5	1.1	0.9	66.3	5.4	1.8	1.8	1.3	2.0	+0.4	-0.7	-1.8
7A	375	5.5	—	2.5	14	0.0	—	1.4	0.1	13.4	0.1	0.9	1.3	82.5	1.9	0.50	0.18	0.76	0.60	-0.6	-1.4	-1.8
7B	375	5.5	16	2.5	22	0.2	—	6.3	0.2	10.6	0.6	1.2	--	77.4*	4.0	5.72	0.26	1.7	1.4	0.0	-0.4	-7.1
7C	375	5.5	4.8	2.5	33	0.3	—	15.5	0.6	6.3	1.3	0.9	0.5	67.0	4.8	1.2	0.54	1.9	2.0	+2.1	+0.8	+2.5
8A	375	5.6	—	1.9	11	0.1	0.0	1.9	0.3	14.5	0.4	0.5	0.6	79.8	1.4	0.26	0.14	0.41	0.53	+2.2	+2.5	-6.8
8B	375	5.5	16	1.9	29	0.1	--	6.4	0.2	11.4	1.5	0.2	0.0	75.3	3.3	0.51	0.60	1.5	1.3	+2.0	+1.8	-9.5
8C	375	5.5	4.8	1.9	30	0.2	--	15.7	0.4	9.6	0.8	0.9	0.3	67.1	2.9	0.60	0.15	1.5	1.3	+3.6	+2.5	-4.8
9A	475	5.5	--	3.4	98	0.0	--	13.3	10.7	0.4	3.[illegible]	4.1	7.2	59.0	20.4	0.41	0.22	0.84	0.94	+0.5	+0.1	+8.7
9B	475	5.6	16	3.1	99	0.3	—	15.3	8.3	0.3	4.2	1.3	5.6	60.8	19.6	0.21	0.08	1.0	1.3	-0.3	-0.9	+4.4
9C	475	5.5	4.8	3.5	87	0.4	—	17.9	6.2	1.8	3.3	0.5	4.7	58.0	15.7	0.30	0.14	0.92	1.2	+3.8	+1.3	-0.5
10A	475	5.6	—	2.5	97	0.2	0.0	12.9	8.7	0.5	3.2	1.9	6.8	62.3	21.8	0.56	0.61	0.61	1.4	-0.8	-2.5	+0.3
10B	475	5.5	16	2.5	97	0.0	—	15.7	9.9	0.5	3.8	2.9	6.9	57.6	19.8	0.19	[illegible]	1.0	[illegible]	[illegible]	[illegible]	+5.3
10C	475	5.5	4.8	2.5	98	0.0	--	[illegible]	7.9	0.3	4.2	1.2	6.9	55.3	15.7	0.30	0.14	0.98	1.1	+1.6	[illegible]	+10.0
11A	475	5.5	--	1.6	38	0.0	—	5.2	0.9	9.9	0.8	1.1	0.7	75.6	5.5	[illegible]	0.51	0.36	0.46	+2.5	+1.5	-3.2
11B	475	5.5	16	1.6	41	0.0	---	9.4	1.1	8.7	0.8	0.5	0.4	72.6	6.1	1.8	0.47	0.53	0.47	+2.6	+1.8	-0.3
11C	475	5.5	4.8	1.6	56	0.0	--	17.2	1.4	5.6	1.0	0.5	0.7	65.0	7.4	1.8	0.82	0.59	0.63	+3.1	+1.1	+3.2
12A	475	5.5	—	2.3	61	0.0	--	8.1	[illegible]	6.2	1.1	1.4	1.0	71.8	11.6	2.1	0.63	0.62	0.89	+2.2	+0.8	-2.8
12B	475	5.6	16	2.3	81	0.1	--	12.4	3.2	2.7	2.1	1.4	2.4	65.6	13.0	2.2	0.87	0.70	1.1	+2.5	+1.4	+0.9
12C	475	5.5	4.8	2.3	90	0.1	—	18.7	5.3	1.4	3.0	0.7	2.4	58.8	13.4	2.0	1.1	0.94	1.1	+4.5	+2.7	+1.9
13A	475	5.4	—	1.2	40	0.0	--	6.4	1.3	9.6	0.6	0.6	2.6	74.6	7.2	1.8	0.46	0.45	0.55	+0.9	0.0	-2.9
13B	475	5.6	16	1.1	96	0.2	—	15.6	12.0	0.5	5.0	2.5	8.7	58.0	18.6	0.10	0.20	0.42	0.72	-1.8	-1.9	+6.5
13C	475	5.6	4.8	1.1	95	0.4	--	22.2	10.8	0.6	5.0	2.0	8.3	56.0	17.1	0.10	0.17	0.44	0.48	-3.9	-5.4	+1.4
14A	475	5.6	—	0.7	19	0.0	—	3.0	0.3	12.5	0.4	0.9	0.7	80.8	2.4	1.1	0.28	0.20	0.23	+0.4	-0.2	-1.5
14B	475	5.6	16	0.7	20	0.0	—	7.4	0.6	11.7	0.2	1.2	0.4	75.7	3.0	1.0	0.26	0.23	0.23	+2.2	+1.3	-3.3
14C	475	5.6	4.8	0.7	21	0.0	--	16.2	0.4	9.7	0.3	1.0	0.2	69.1	2.5	0.81	0.36	0.27	0.24	+1.1	+1.6	+4.9
15A	425	5.4	—	3.9	11	0.0	—	1.9	0.1	14.2	0.0	0.7	--	79.9*	1.5	0.73	0.05	0.30	0.07	+2.8	+2.6	-2.6
15B	425	5.5	16	4.0	22	0.0	--	6.7	0.1	11.8	0.3	0.7	0.3	75.0	3.0	1.2	0.32	0.59	0.01	+2.9	+2.6	-3.7
15C	425	5.5	4.8	4.0	46	0.0	—	15.8	0.5	7.1	0.8	0.8	--	65.6*	5.2	1.7	0.47	1.2	0.48	+3.3	+2.4	-2.1
16A	425	5.5	--	6.0	31	0.0	--	4.3	0.4	10.4	0.6	0.6	--	76.1*	4.5	1.9	0.38	0.62	0.29	+0.4	+0.3	-1.3
16B	425	5.5	16	6.0	46	0.1	--	8.4	0.6	7.9	0.6	0.4	0.7	70.9	6.1	2.2	0.34	1.2	0.52	+3.0	+2.0	-1.4
16C	425	5.6	4.8	6.0	88	0.2	—	16.3	1.3	1.4	2.1	0.7	0.3	61.7	9.9	2.5	0.59	1.9	1.0	-0.4	+2.6	+0.8
17A	425	5.5	--	8.0	54	0.0	--	6.5	0.8	6.5	1.0	1.2	0.4	72.0	6.6	2.9	1.0	0.59	0.56	-1.4	-2.0	0.0
17B	425	5.5	16	8.0	81	0.0	--	10.2	1.3	2.3	1.8	0.4	--	67.9*	9.9	[illegible]	1.4	0.78	0.86	-1.7	-3.3	+3.7
17C	425	5.6	4.9	7.9	94	0.3	0.0	16.5	1.9	0.5	3.2	0.9	1.3	58.3	11.6	2.2	1.0	1.2	1.1	+0.9	-1.2	-1.0
18A	425	5.8	--	12.0	95	0.3	--	9.5	3.6	0.7	2.7	2.5	3.7	58.6	12.2	2.7	1.3	0.68	0.79	-0.8	-2.0	-1.0
18B	425	5.6	17	10.1	96	0.2	—	11.0	2.3	0.4	3.1	1.0	—	62.9*	14.1	1.9	1.2	0.55	1.1	-2.4	+1.2	-1.0
18C	425	5.5	4.7	2.0	14	0.0	--	15.1	0.2	11.1	0.2	0.7	0.1	69.8	1.7	0.57	0.25	0.17	0.11	-0.8	-1.9	-2.1
19A	425	5.5	—	10.0	87	0.1	--	8.7	1.5	1.7	2.0	1.6	1.6	64.7	12.3	3.2	0.30	1.6	0.80	-0.7	-2.3	+2.2
19B	425	5.5	16	5.1	29	0.1	--	7.3	0.5	10.3	0.4	0.7	0.1	73.8	3.6	1.4	0.14	0.79	0.27	+0.8	+0.4	-3.0
19C	425	5.5	4.8	5.1	69	0.2	--	16.7	0.7	4.5	1.4	1.0	0.5	62.7	7.9	2.2	0.7	1.6	0.75	+1.3	0.0	-0.7

* Includes Methane ** Includes Methane and Hydrogen *** Includes Hydrogen

TABLE 3

Product Yield Based On Oxygen Reacted

Run No.	Temperature	Produce Yield Moles Per Mole of Oxygen Reacted											
		CO_2	C_2H_2	C_2H_6	C_2H_4	CO	H_2	CH_4	H_2O	H_2O_2	CH_3CHO	HCHO	CH_3OH
4A	375	0.04	--	0.30	0.07	0.31	0.08	--	0.77	0.11	0.054	0.24	0.33
4B	375	0	--	0.53	0.07	0.32	--	--	0.76	0.11	0.024	0.27	0.40
4C	375	0.03	--	1.17	0.05	0.35	0.05	0.08	0.73	0.10	0.072	0.27	0.31
5A	375	0.01	--	0.38	0.05	0.21	0.10	0.16	0.84	0.18	0.14	0.20	0.27
5B	375	0.01	--	0.68	0.10	0.25	0.06	0.06	0.70	0.19	0.12	0.21	0.28
5C	375	0.04	--	1.29	0.08	0.30	0.02	0.08	0.68	0.18	0.13	0.21	0.23
6A	375	0.02	--	0.48	0.12	0.15	0.15	0.24	0.82	0.23	0.15	0.19	0.21
6B	375	0	--	1.30	0.10	0.23	0.16	0	0.73	0.22	0.15	0.19	0.27
6C	375	0.02	--	2.00	0.18	0.19	0.14	0.11	0.68	0.22	0.22	0.16	0.26
7A	375	0	--	0.63	0.04	0.05	0.41	0.57	0.66	0.23	0.08	0.34	0.25
7B	375	0.04	--	1.26	0.04	0.12	0.23	--	0.80	0.16	0.05	0.34	0.29
7C	375	0.04	--	2.19	0.08	0.18	0.13	0.37	0.68	0.17	0.08	0.27	0.28
8A	375	0.05	0.0	1.08	0.18	0.23	0.34	0.33	0.83	0.15	0.08	0.24	0.31
8B	375	0.02	--	1.38	0.04	0.33	0.04	0	0.72	0.11	0.13	0.32	0.28
8C	375	0.05	--	3.8	0.09	0.18	0.20	0.08	0.70	0.14	0.04	0.35	0.30
9A	475	0	--	0.98	0.79	0.28	0.30	0.54	1.51	0.030	0.016	0.062	0.069
9B	475	0.02	--	1.13	0.62	0.31	0.09	0.43	1.45	0.016	0.0060	0.075	0.093
9C	475	0.03	--	1.57	0.55	0.29	0.08	0.41	1.39	0.027	0.012	0.082	0.11
10A	475	0.01	0.0	0.89	0.61	0.22	0.13	0.47	1.50	0.038	0.042	0.042	0.093
10B	475	0	--	1.19	0.75	0.29	0.22	0.52	1.50	0.14	0.013	0.076	0.093
10C	475	0	--	1.79	0.59	0.37	0.11	0.60	1.38	0.026	0.012	0.086	0.096
11A	475	0	--	0.87	0.16	0.15	0.18	0.12	0.92	0.36	0.086	0.061	0.077
11B	475	0	--	1.56	0.18	0.13	0.09	0.07	1.02	0.31	0.079	0.086	0.079
11C	475	0	--	2.47	0.20	0.14	0.08	0.10	1.06	0.25	0.12	0.085	0.090
12A	475	0	--	0.85	0.20	0.12	0.14	0.10	1.21	0.22	0.067	0.065	0.094
12B	475	0.01	--	1.10	0.29	0.19	0.12	0.21	1.15	0.20	0.077	0.061	0.094
12C	475	0.01	--	1.57	0.28	0.25	0.06	0.20	1.12	0.17	0.092	0.079	0.090
13A	475	0	--	0.99	0.20	0.10	0.09	0.40	1.11	0.28	0.071	0.069	0.085
13B	475	0.02	--	1.22	0.94	0.39	0.19	0.67	1.45	0.01	0.016	0.033	0.056
13C	475	0.03	--	1.83	0.89	0.41	0.17	0.68	1.41	0.01	0.015	0.036	0.039
14A	475	0	--	1.03	0.11	0.14	0.30	0.24	0.81	0.39	0.097	0.067	0.078
14B	475	0	--	2.50	0.20	0.07	0.39	0.13	1.00	0.34	0.087	0.079	0.076
14C	475	0	--	6.12	0.15	0.12	0.36	0.08	0.94	0.31	0.14	0.097	0.091
15A	425	0	--	1.08	0.06	0	0.38	--	0.88	0.42	0.021	0.11	0.04
15B	425	0	--	2.04	0.04	0.08	0.21	--	0.91	0.37	0.10	0.18	0.03
15C	425	0	--	2.68	0.09	0.14	0.14	0.11	0.88	0.29	0.08	0.21	0.08
16A	425	0	--	0.91	0.08	0.12	0.14	--	0.95	0.41	0.08	0.13	0.06
16B	425	0.01	--	1.24	0.09	0.09	0.07	0.11	0.90	0.33	0.05	0.18	0.08
16C	425	0.01	--	1.56	0.12	0.22	0.06	0.02	0.94	0.24	0.06	0.18	0.10
17A	425	0	--	0.82	0.11	0.12	0.15	0.06	0.84	0.37	0.13	0.07	0.07
17B	425	0	--	0.98	0.13	0.18	0.04	--	0.95	0.31	0.13	0.07	0.08
17C	425	0.02	0.0	1.45	0.17	0.28	0.08	0.12	1.02	0.19	0.09	0.10	0.09
18A	425	0.03	--	0.78	0.30	0.22	0.21	0.31	1.0	0.23	0.11	0.06	0.07
18B	425	0.02	--	0.89	0.19	0.25	0.08	--	1.15	0.16	0.10	0.04	0.09
18C	425	0	--	8.3	0.11	0.11	0.40	0.04	0.95	0.31	0.14	0.09	0.06
19A	425	0.01	--	0.76	0.13	0.17	0.14	0.14	1.07	0.28	0.03	0.14	0.07
19B	425	0.02	--	1.75	0.11	0.09	0.16	0.02	0.86	0.34	0.03	0.19	0.07
19C	425	0.02	--	2.04	0.08	0.17	0.12	0.03	0.85	0.27	0.08	0.19	0.09

hydrogen peroxide isolated per mole of propane reacted reached a maximum at 425°C, as shown in Figures 2 and 3. At 475°C, the amount of oxygenated organics formed per quantity of propane reacting had further decreased, the amount of propylene began to decrease, and the amount of ethylene and methane increased. The products are primarily water and olefins.

Inlet Propylene Concentration

At all temperatures investigated, when the inlet propylene concentration was increased, the induction period of the reaction decreased although the overall rate of oxygen consumption was not significantly changed. Figures 4, 5, and 6 show the extent of reaction as a function of residence time at 375, 425, and 475°C for different inlet propylene concentrations. The figure given as per cent of the inlet oxygen reacted, was calculated by dividing the total of the oxygen atoms found in the product less the unreacted oxygen atoms in the oxygen gas as such in the product, by the total of the oxygen atoms found in the product, this number being multiplied by 100.

The quantities of acetaldehyde, formaldehyde, methanol, and water found per mole of oxygen reacted increased somewhat when propylene was added. Three typical plots are presented in Figures 7, 8, and 9, showing the effect of inlet propylene concentration on the amounts of acetaldehyde, formaldehyde, and methanol isolated per mole of oxygen reacted. The quantity of hydrogen peroxide isolated per mole of oxygen reacted usually decreased as the inlet propylene concentration was increased as is shown in Figure 10. The sum of the water plus hydrogen peroxide isolated per mole of oxygen reacted was not significantly affected by propylene addition.

Some of the diluent propylene may have reacted at 375°C since the amount of propylene isolated at this temperature was much lower than that predicted from the total of the propylene added and the propylene which would be expected to be formed from the propane-oxygen reaction.

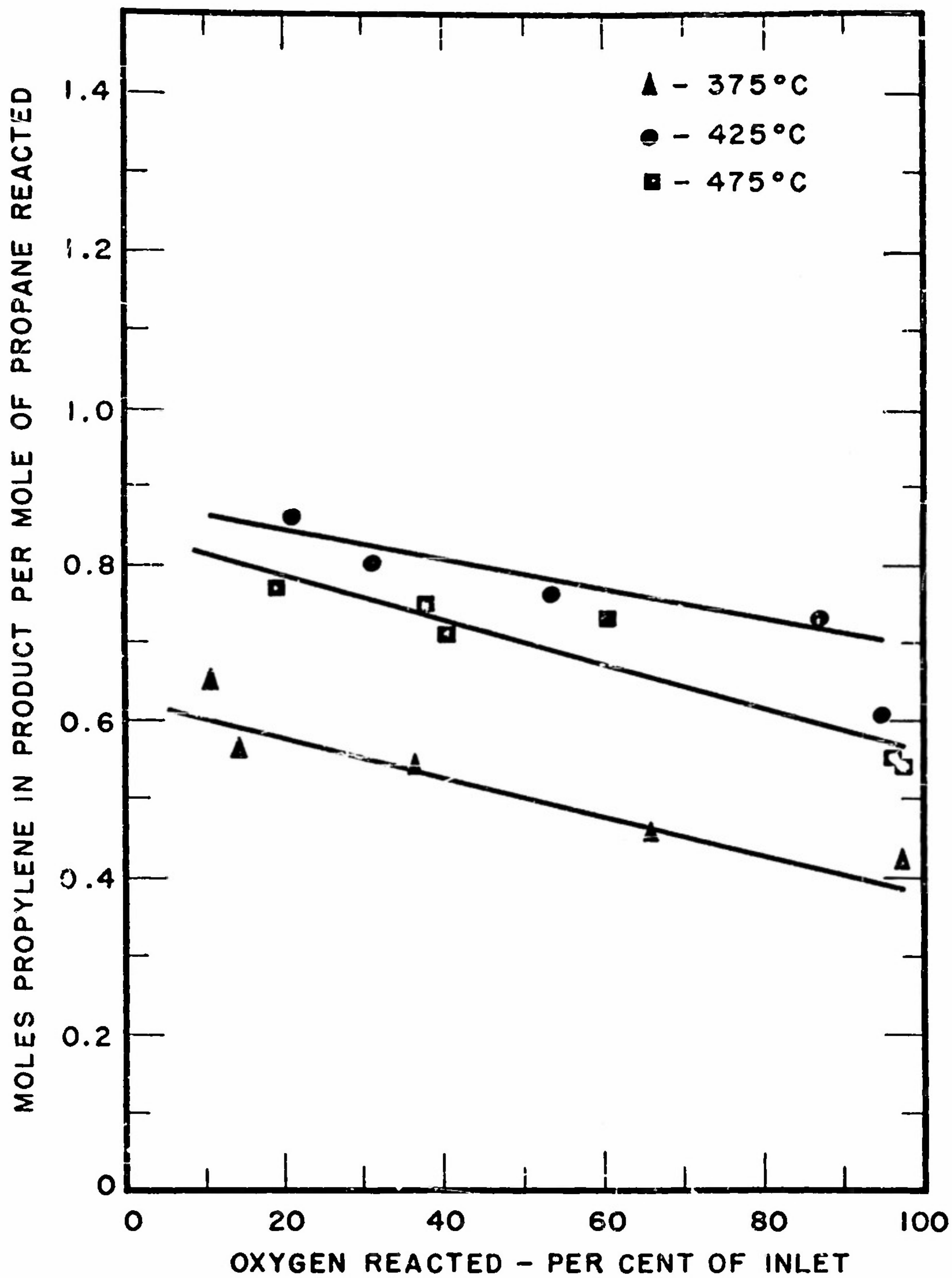

FIGURE 2

YIELD OF PROPYLENE IN ABSENCE OF ADDED PROPYLENE.

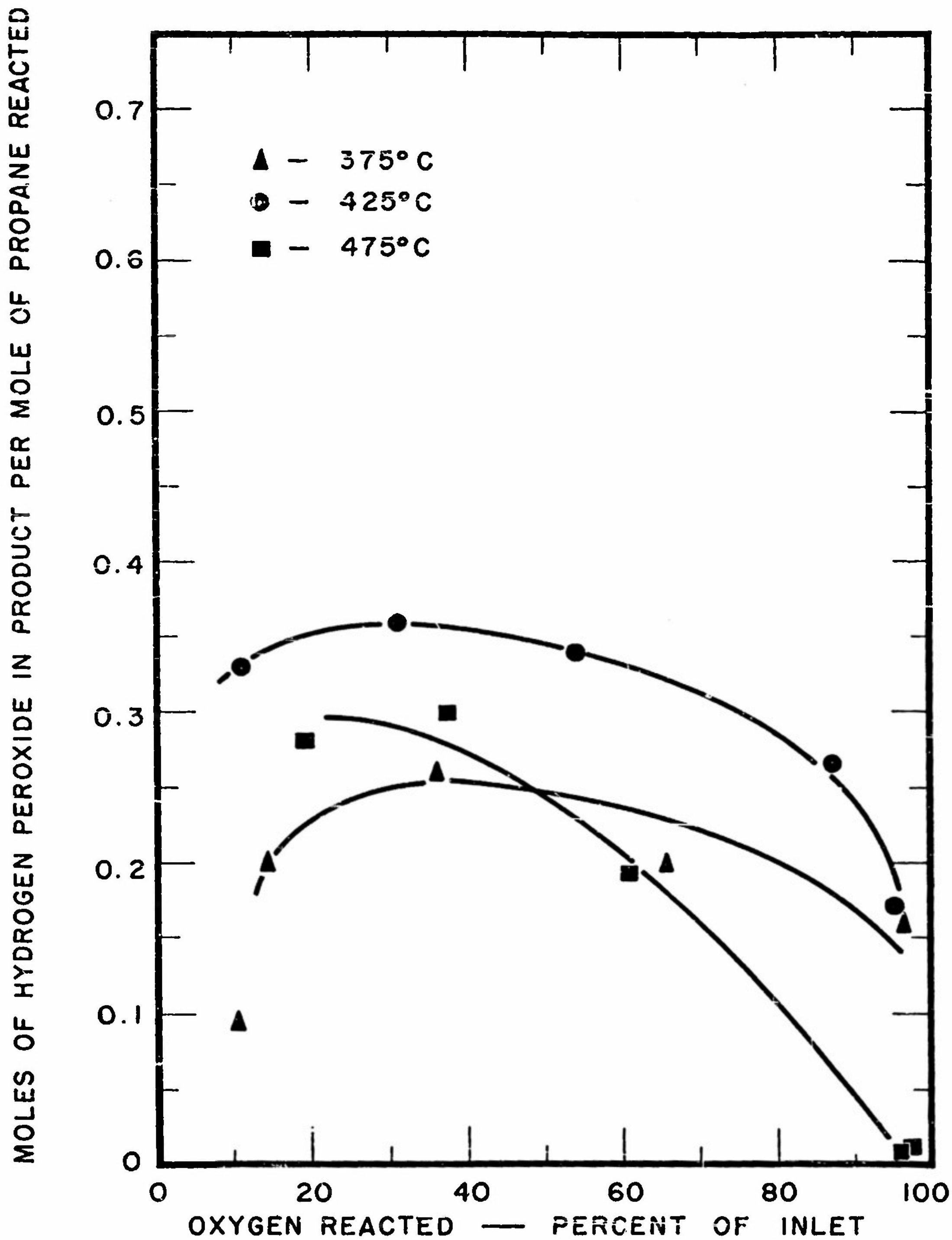

FIGURE 3

YIELD OF HYDROGEN PEROXIDE IN ABSENCE OF ADDED PROPYLENE.

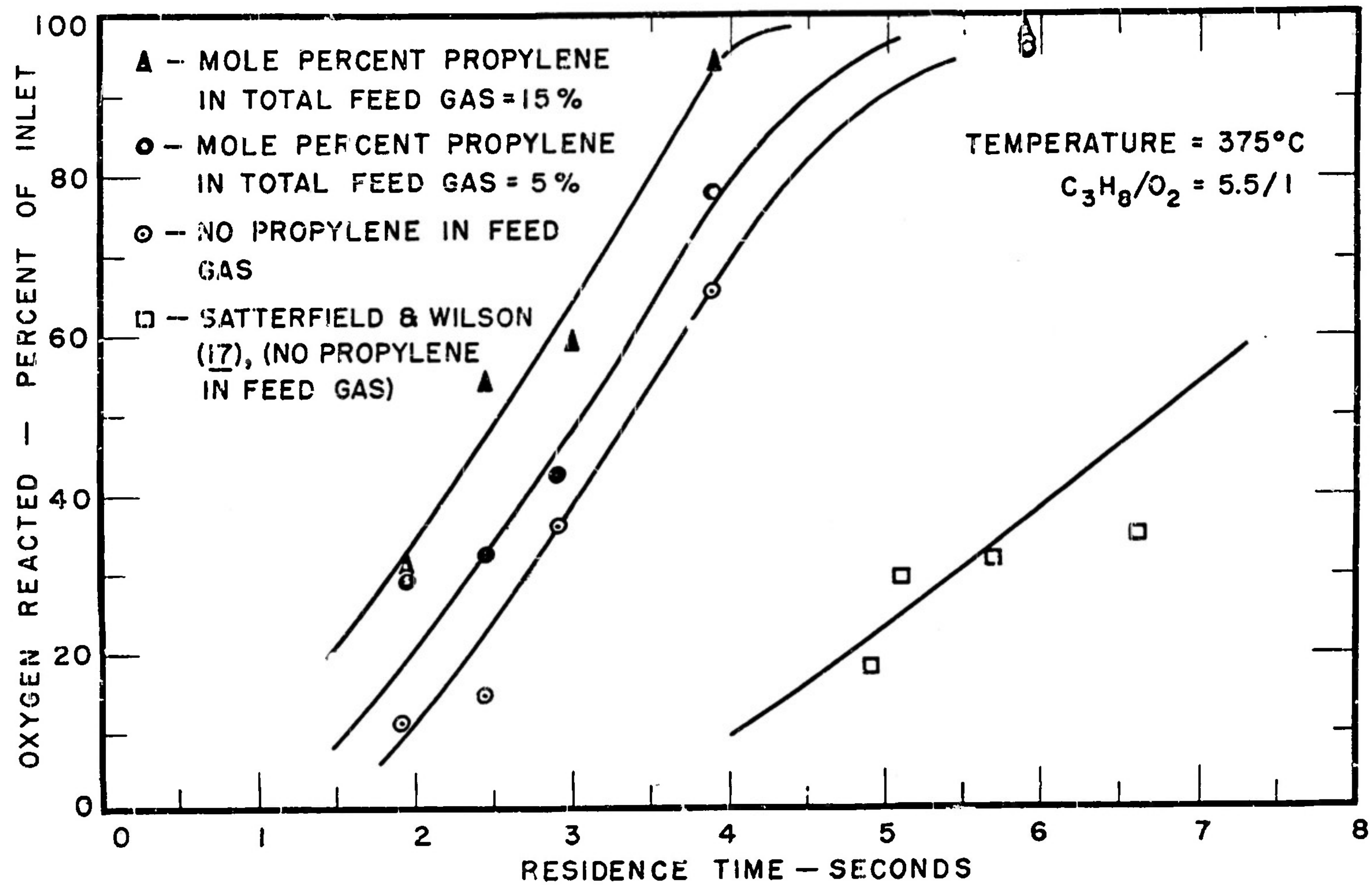

FIGURE 4

EFFECT OF ADDED PROPYLENE ON RATE OF REACTION — 375°C

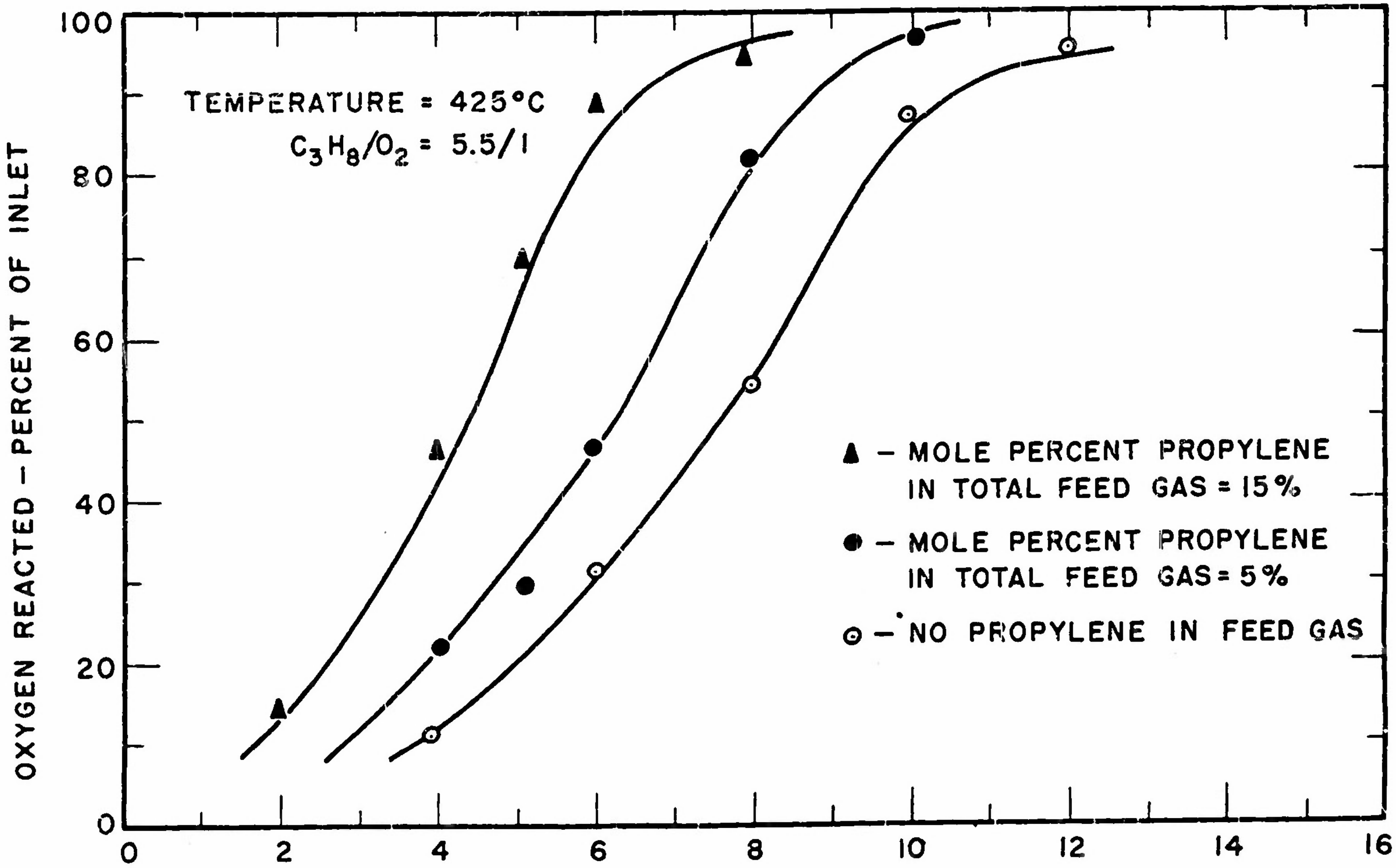

FIGURE 5

EFFECT OF ADDED PROPYLENE ON RATE OF REACTION — 425° C

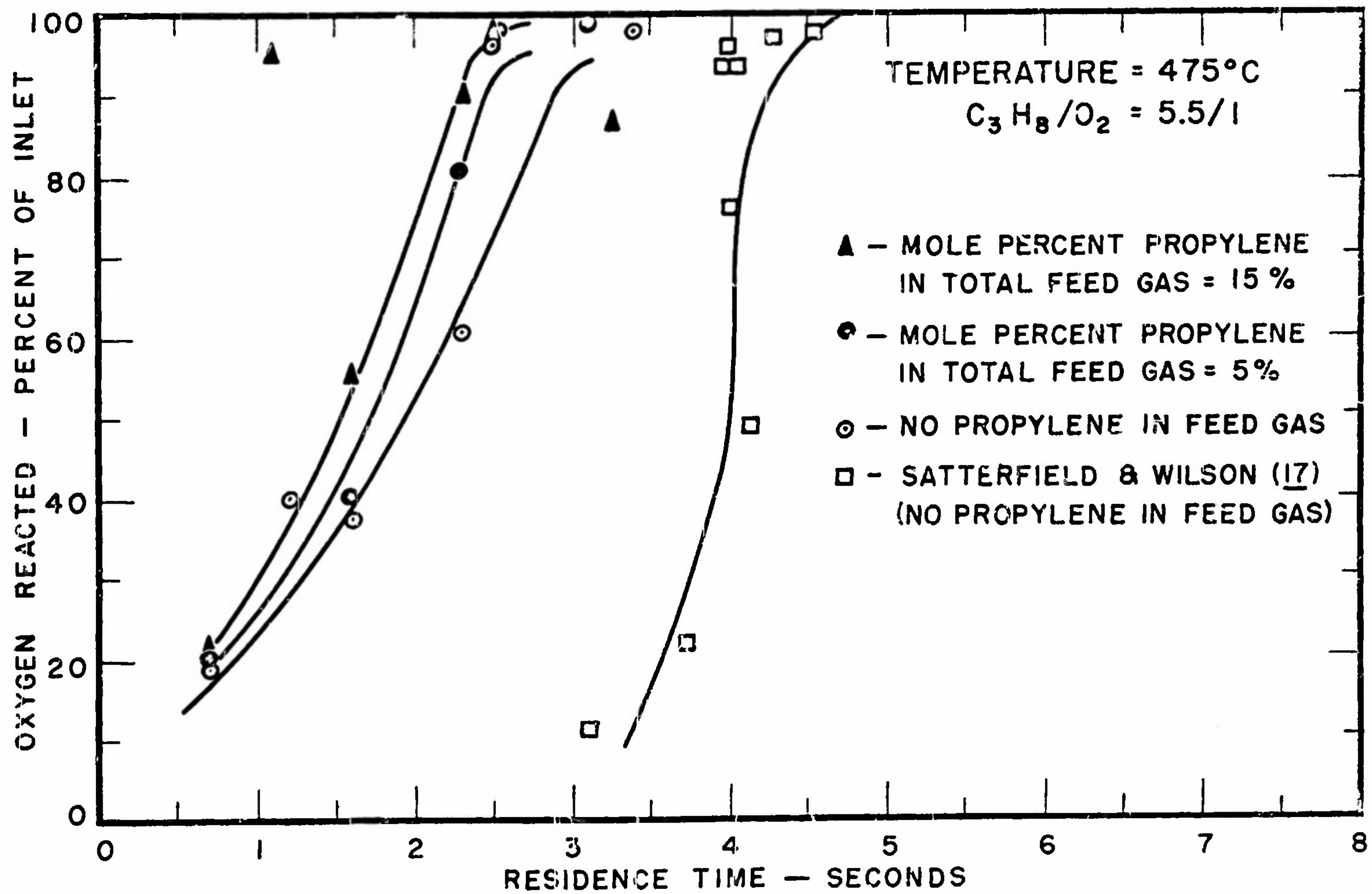

FIGURE 6

EFFECT OF ADDED PROPYLENE ON RATE OF REACTION — 475°C

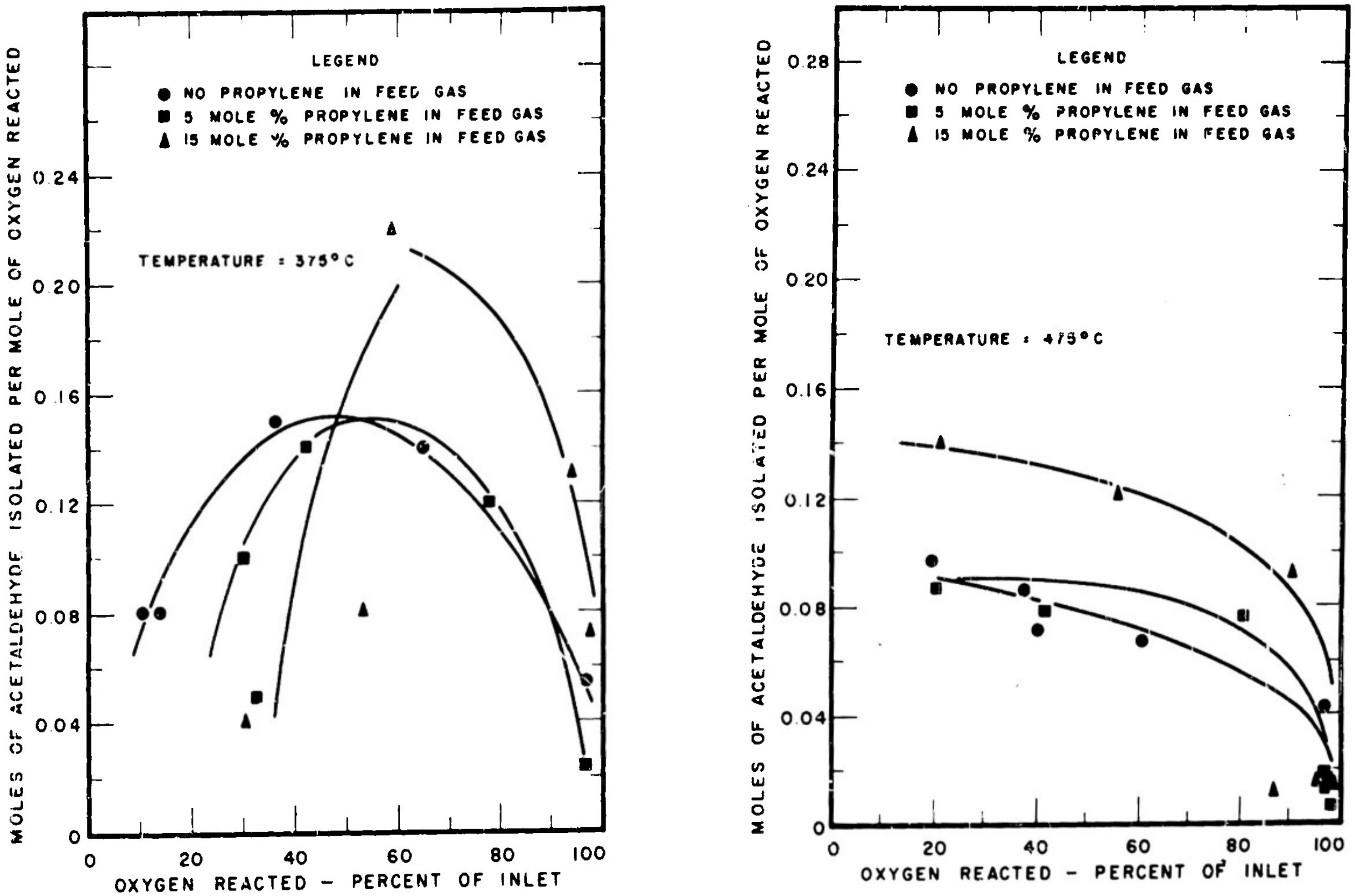

FIGURE 7

EFFECT OF PROPYLENE ON THE VARIATION OF MOLES OF ACETALDEHYDE ISOLATED PER MOLE OF OXYGEN REACTED

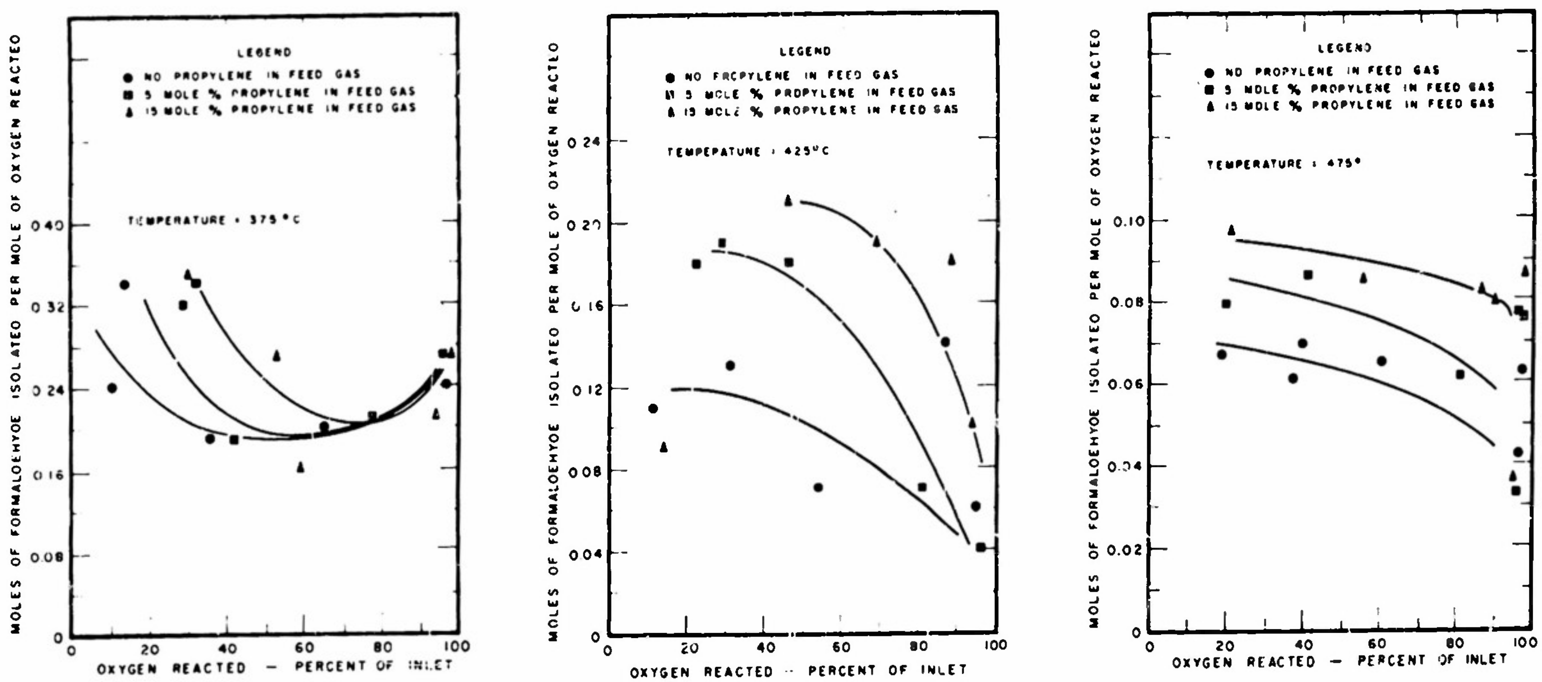

FIGURE 8

EFFECT OF PROPYLENE ON THE VARIATION OF MOLES OF FORMALDEHYDE ISOLATED PER MOLE OF OXYGEN REACTED

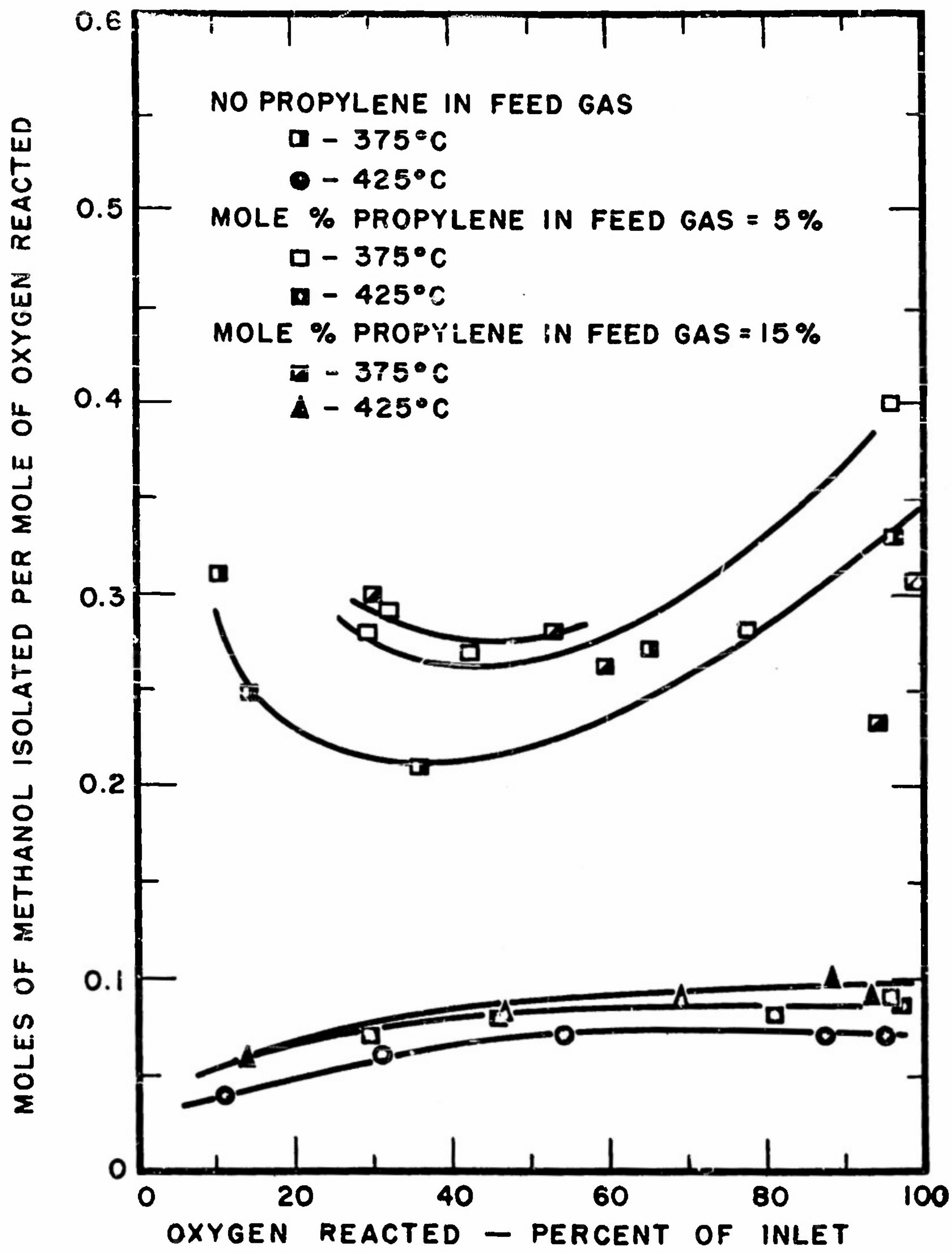

FIGURE 9

EFFECT OF PROPYLENE ON THE AMOUNT OF METHANOL ISOLATED.

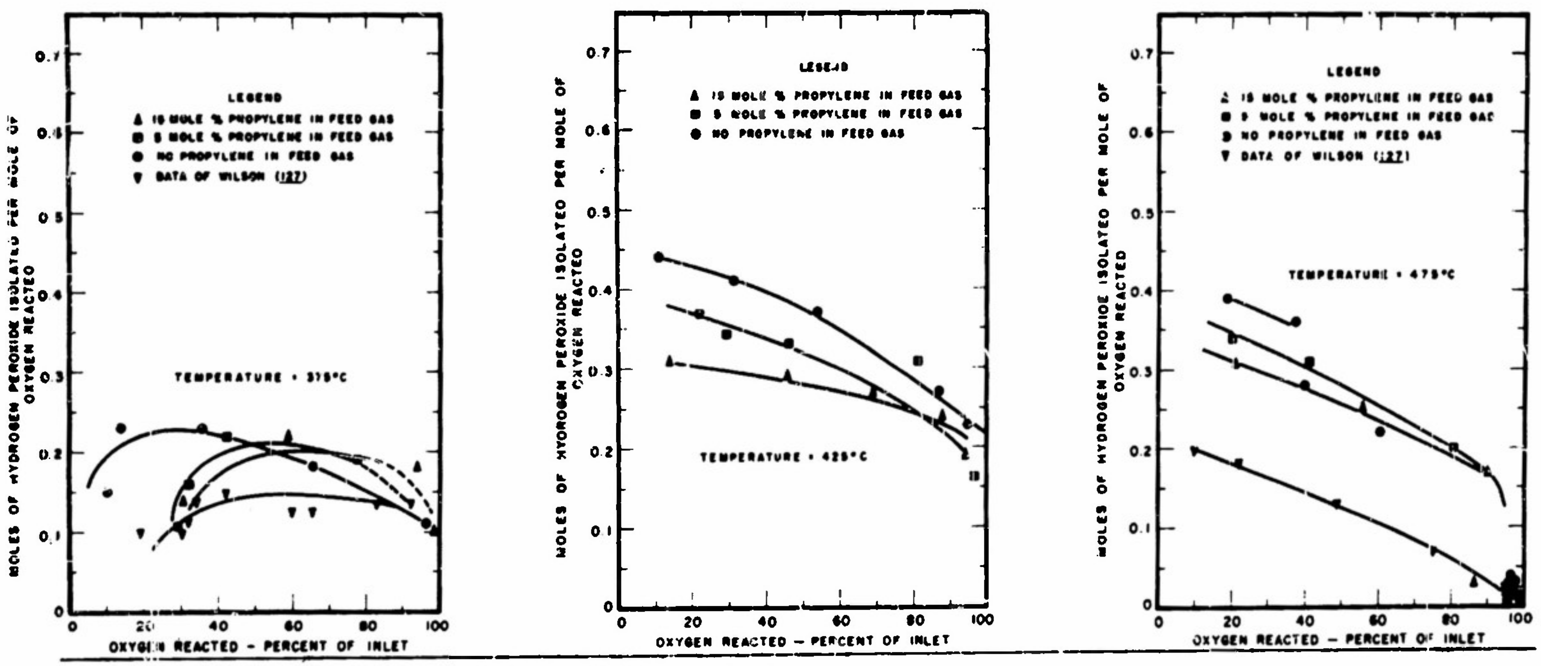

FIGURE 10

EFFECT OF PROPYLENE ON THE VARIATION OF MOLES OF HYDROGEN PEROXIDE ISOLATED PER MOLE OF OXYGEN REACTED

In each group of three runs, as more propylene was added, the propane-oxygen flow rates were reduced. This, in effect, gave a higher total hydrocarbon-to-oxygen mole ratio. It has been reported (16) that such an increase in the hydrocarbon-to-oxygen mole ratio of itself increases the oxidation rate, even at very high ratios. This is not the case here, as shown by the results of two additional runs in which additional propane was added instead of propylene. Compared to runs with a lower propane-oxygen ratio, the additional propane was found to give only a slightly increased degree of reaction, much less than the effect of propylene. It was therefore concluded that the increased amount of reaction occuring when propylene was added was due to a specific chemical effect and not to the increased hydrocarbon-to-oxygen ratio as such.

Extent of Reaction

The quantities of methanol, the carbon oxides, ethylene, water, and methane found in the products per mole of oxygen reacted generally increased as the per cent of the inlet oxygen reacted increased. The effect is particularly striking for methane, as shown in Figure 11 for 475°C. The yields of acetaldehyde, formaldehyde, and hydrogen peroxide per mole of oxygen reacted sometimes increased to a maximum as the reaction progressed but always rapidly decreased as the percent oxygen reacted approached 100%.

The maximum yield of hydrogen peroxide expressed as moles isolated per mole of oxygen reacted was found to be 0.42 at 425°C with 11% of the inlet oxygen reacted; the maximum concentration of hydrogen peroxide in the exit gas was found to be 3.3 mole % at 425°C with 87% of the inlet oxygen reacted.

A 5.5 to 1 molar mixture of pure propylene and oxygen was also allowed to react in two runs, one at 375°C and one at 475°C. The results of these experiments are presented in Table 4. The same qualitative distribution of products was found as in the oxidation of propane alone. In addition to the aqueous condensate produced, a yellow-brown oil layer was formed which was undoubtedly a propylene polymer. Material balances indicated that at 375°C

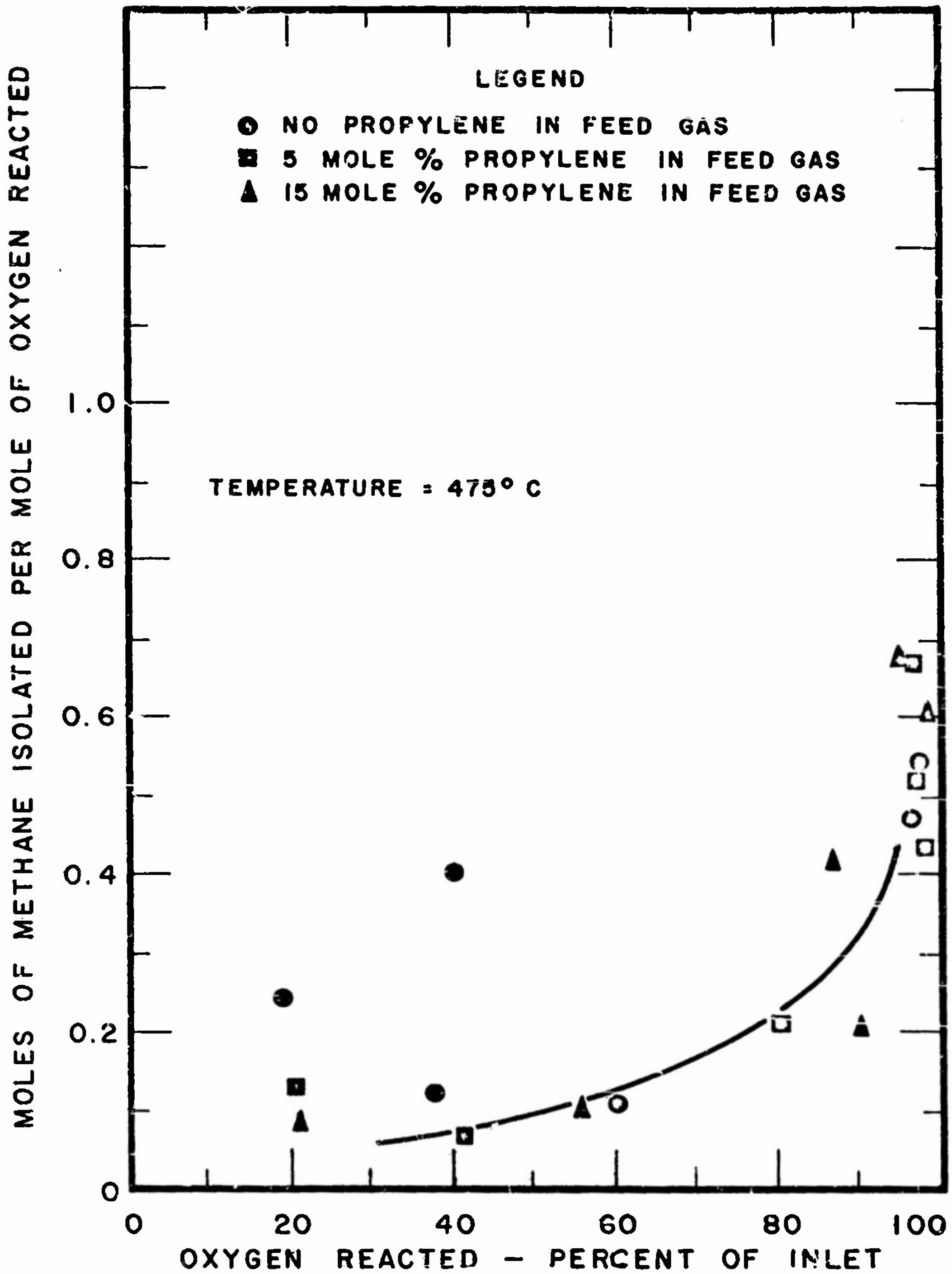

FIGURE II

EFFECT OF OXYGEN CONCENTRATION ON MOLES OF METHANE ISOLATED.

TABLE 4

Results of Experimental Runs in Which Only Propylene was Oxidized

Temperature	375°C	475°C
Mole Ratio (C_3H_6/O_2)	5.4	4.8
Residence Time-sec.	12	8.8
% Inlet Oxygen Reacted	38	89
Moles of Product per 100 moles of Entering Gas		
CO_2	0.0	0.0
C_2H_2	0.0	2.6
C_3H_6	75.48	20.91
C_2H_4	0.0	21.20
O_2	9.99	2.73
CO	1.50	5.83
H_2	0.0	1.39
CH_4	not analyzed for	
H_2O	3.31	30.79
H_2O_2	1.61	1.39
CH_3CHO	2.65	2.20
HCHO	1.15	3.66
CH_3OH	0.93	0.58
Material Balances*		
Carbon	+6.0	+28
Hydrogen	+3.2	-5.9
Oxygen	-5.2	-47

* Defined as $\frac{\text{atoms in} - \text{atoms out}}{\text{atoms in}} \times 100$ but excluding oil layer formed

about 6%, and at 475°C, about 28% of the carbon in the propylene reacting appeared as this polymer. A significant fact was that much longer contact times were required to consume a given fraction of the inlet oxygen when it is reacting with pure propylene than with pure propane. However, mixtures of propane and propylene reacted faster than either species alone.

DISCUSSION OF RESULTS

When propane alone is oxidized, propylene is a major product. Since this propylene acts similarly to any added propylene, the experimental results must be interpreted on a relative basis, i.e., the effect of added propylene on the induction period, reaction rate, and product distribution will only magnify any effects which may be due to propylene in the undiluted case. The discussion presented here will attempt to outline a mechanism of propane oxidation emphasizing the reactions in which propylene plays an important role. Various reaction steps which may be involved in propane oxidation are presented in Figure 12. Many other paths not shown are also possible, but the scheme may help to orient the reader in the following discussion.

Initiating Reactions

In a propane and oxygen mixture at high temperature, the initial fission of the propane molecule can occur either by thermal cracking or by attack from an oxygen molecule. Thermal cracking is not considered to be important for the following reasons. Experimentally, when propane and nitrogen (instead of oxygen) were preheated and passed through the reactor, no products of cracking were detected until a temperature of 475°C was reached. At this temperature, only about 0.1 to 0.2 per cent of the inlet propane was found to decompose, forming predominantly hydrogen and propylene. This small amount of cracking has of itself a negligible effect on the product distribution obtained. The free radicals produced in the cracking reaction are not important in initiating the reaction since it is known that propylene inhibits the thermal decomposition of propane (15), yet propylene added to a propane-oxygen mixture was found to decrease the induction

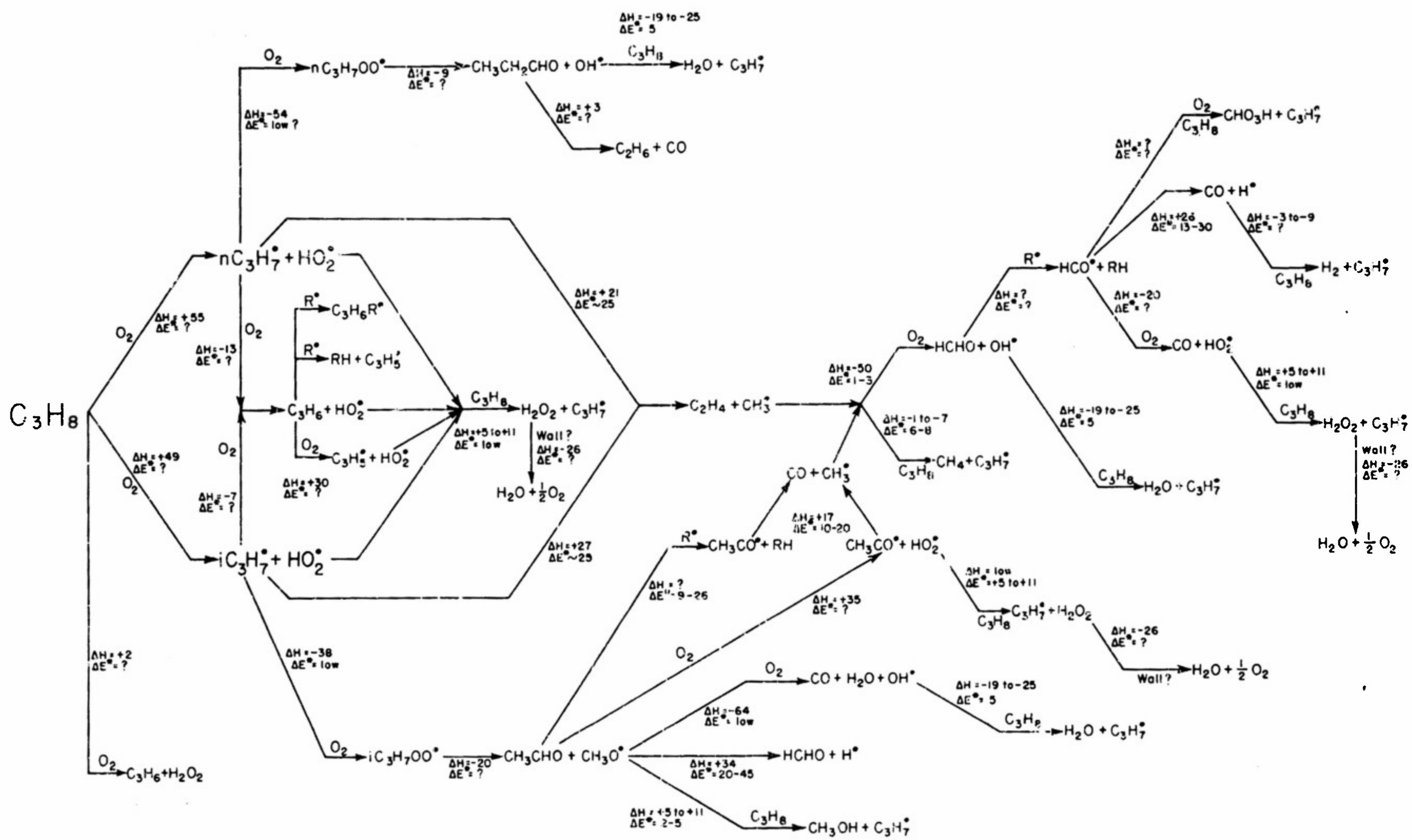

FIGURE 12 – AN OUTLINE OF REACTION STEPS IN PROPANE OXIDATION.

inhibiting action of propylene in free-radical reactions is attributable to its reaction with reactive free radicals as in equation (2) producing a resonance-stabilized inactive allyl radical. This long lived radical may, in fact, combine with another to produce diallyl, the net result of which is the removal of two reactive chain carriers per molecule of diallyl formed.

When propylene is added initially to the propane and oxygen mixture, the oxygen will preferentially attack the propylene since it has the weakest carbon-hydrogen bond.

$$C_3H_6 + O_2 \longrightarrow C_3H_5^{\bullet} + HO_2^{\bullet} \qquad (3)$$

The products of reaction (3) should be able to attack propane with more ease than oxygen.

$$C_3H_8 + HO_2^{\bullet} \longrightarrow C_3H_7^{\bullet} + H_2O_2 \qquad (4)$$

$$C_3H_8 + C_3H_5^{\bullet} \longrightarrow i\text{-}C_3H_7^{\bullet} + C_3H_6 \qquad (5)$$

To summarize the initiating steps in the reaction: if no propylene were present, the initiating reaction is presumably reaction (1) which is slow and explains the induction period found experimentally; if propylene be added to the reacting mixture of propane and oxygen, reactions (3), (4), and (5) eclipse reaction (1) as the initial reaction steps, thereby decreasing the induction period. Propylene, whether produced as a product of the reaction between propane and oxygen or added as a diluent, would act similarly in the initiating steps.

Reactions of the Propyl Radical

The various reactions of the propyl radical have been thoroughly discussed in a recent report (17) and will be but briefly reviewed here.

It is postulated that essentially all the products isolated from propane oxidation are formed by reactions of the propyl radical which may proceed by three paths, the predominating reaction being determined by the temperature.

1. The propyl radicals may thermally decompose to ethylene and methyl radicals.

$$C_3H_7^{\bullet} \longrightarrow C_2H_4 + CH_3^{\bullet} \qquad (6)$$

From a consideration of the bond dissociation energies of the carbon-carbon and carbon-hydrogen bonds in the propyl radical (21), plus the fact that very little hydrogen was found here, it is concluded that only a negligible fraction of the propyl radicals thermally decomposed to form propylene and hydrogen atoms. This conclusion is supported by experimental data on the products of cracking of the propyl radical (20).

2. Propyl radicals may react with oxygen according to reaction (7):

$$C_3H_7^{\bullet} + O_2 \longrightarrow C_3H_6 + HO_2^{\bullet} \qquad (7)$$

3. The propyl radical may react with oxygen to form the propyl peroxide radical which in turn can lead to the formation of the oxygenated organic species, acetaldehyde, formaldehyde, and methanol.

$$C_3H_7^{\bullet} + O_2 \longleftrightarrow \text{oxygenated species} \qquad (8)$$

Reaction (6) becomes important at very high temperatures, i.e. over 500°C. At lower temperatures reaction (7) predominates; the maximum yield of propylene per mole of propane reacting was found at 425°C. Further decrease in temperature increases the importance of reaction (8) and decreases that of reaction (7), thus increased quantities of oxygenated organic species are found and decreased quantities of propylene.

It may be shown that the ratio (moles of propylene/moles of propane forming oxygenated organics) is almost constant at any one temperature for varying degrees of completion of reaction. The constancy of this ratio implies that little or no propylene, once formed in the reaction, reacts further. This ratio does decrease somewhat at 375°C indicating that at this temperature propylene reacts further forming some of the oxygenated organic products. Any reaction involving propylene probably proceeds through the allyl radical which is resonance stabilized and reacts more slowly than the other free radicals participating in the oxidation.

There is no general agreement as to the subsequent reactions of the propyl peroxide radicals, formed in reaction (7), and the results obtained here do not contribute further evidence. The mechanism postulated by Lewis and von Elbe (9) is used in Figure 12, but alternately the peroxide radicals may react with the alkyl radical or another peroxy radical to form an alkoxy radical, as postulated by Bell, Raley, Rust, Seubold, and Vaughan (1).

Formation of Methanol

The methanol formed in the reaction is attributed to the reaction of the methoxy radical, $CH_3O^{\cdot}$, with propane or propylene.

$$CH_3O^{\cdot} + C_3H_8 \longrightarrow CH_3OH + C_3H_7^{\cdot} \qquad (9)$$

The methoxy radical may also react with oxygen in a competing reaction.

$$CH_3O^{\cdot} + O_2 \longrightarrow CO + H_2O + OH^{\cdot} \qquad (10)$$

Experimental evidence for the existence here of this pair of competing reactions comes from noting that the yield of methanol per mole of oxygen reacted increased as the reaction progressed, i.e., as the concentration of oxygen decreased. Adding propylene to the propane-oxygen mixture increased the methanol isolated per mole of oxygen reacted. This is consistent with the hypothesis that propylene, possessing an easily extractable hydrogen, should increase the amount of reaction (9) relative to reaction (10), thus leading to the higher yields of methanol.

Reactions of Acetaldehyde

Acetaldehyde is not a stable intermediate; only a fraction of the total amount presumably formed from the decomposition of the isopropyl peroxide radical is found in the products. One way it may disappear is by reaction with free radicals.

$$CH_3CHO + R^{\cdot} \longrightarrow CH_3CO^{\cdot} + RH \qquad (11)$$

The acetyl radical is unstable (7, 19) and readily decomposes.

$$CH_3CO^{\cdot} \longrightarrow CH_3^{\cdot} + CO \qquad (12)$$

It has been realized for some time that oxygen catalyzes the free-radical decomposition of acetaldehyde (10, 11, 12, 13, 23) so it appears plausible to insert a competing oxidation reaction with the straight free-radical decomposition reaction.

$$CH_3CHO + O_2 \longrightarrow CH_3CO^{\bullet} + HO_2^{\bullet} \qquad (13)$$

In reaction (13) the hydrogen atom attached to the carbonyl carbon is considered more labile, but this view has been disputed (4, 5). The principal difference between reactions (11) and (13) is that the former is a straight chain-continuing reaction while the latter is chain-branching. The branching-chain characteristics of reaction (13) predict that the higher the concentration of acetaldehyde and oxygen in a propane-oxygen system, the more rapid the reaction. Until recently the effects noted when acetaldehyde was added to the original propane-oxygen system at low temperatures was one of decreasing the induction period and increasing the rate of the oxidation (8, 14). This agrees well with prediction. However, recent work (18) has indicated that this rate-accelerating effect of acetaldehyde is not present at the higher temperatures. The tentative conclusion may be drawn that at the low temperatures, the branching reaction of acetaldehyde predominates, but as the temperature is increased the free-radical non-branching reaction increases in importance. This view leads one to postulate that this change in mechanism is the cause of the decreasing rate region noted between 400 and 425°C. In the same temperature region, there is also a decreasing amount of acetaldehyde formed with increased temperature, as discussed previously, which likewise decreases the effect of the oxidation reaction.

The effect of propylene on these two reactions would be to increase the amount of acetaldehyde found in the products by (a) decreasing the active free-radical concentration (reaction (2)), and (b) by reaction with the acetyl radical to reform acetaldehyde. The experimental data indicate that the yield of acetaldehyde per mole of oxygen reacted usually does increase with the addition of more propylene as shown in Figure 7.

Reactions of the Methyl Radical

The methyl radicals, formed from the decomposition of the acetyl and propyl radicals, may react in two ways.

$$CH_3\cdot + C_3H_8 \longrightarrow CH_4 + C_3H_7\cdot \qquad (14)$$

$$CH_3\cdot + O_2 \longrightarrow HCHO + OH\cdot \qquad (15)$$

There is some question about the exact mechanism of reaction (15) (11, 20), as no spectroscopic OH bands have been noted in oxidation studies of the methyl radical (3).

Figure 11 shows that the methane yield per mole of oxygen reacting increases as the concentration of oxygen decreases, as would be predicted. However the effect of propylene on the methane yield is not as pronounced as might have been expected from the analogous case involving the methoxy radical. Undoubtedly propylene does provide a readily extractable source of hydrogen in reaction (14) which should increase the rate of this reaction, however propylene may also react with methyl radicals in an addition reaction (22).

$$CH_3\cdot + C_3H_6 \longrightarrow C_4H_9\cdot \qquad (16)$$

The net effect of propylene is thus small as both reactions tend to counterbalance each other.

Reactions of Formaldehyde

Formaldehyde decomposes primarily by a free-radical mechanism similar to that proposed for acetaldehyde.

$$HCHO + R\cdot \longrightarrow CHO\cdot + RH \qquad (17)$$

The experimental data show that propylene addition increases the amounts of formaldehyde found in the products, as shown in Figure 8. Propylene presumably inhibits the decomposition of formaldehyde by regeneration of formaldehyde from the peroxyformyl radical and by decreasing the free-radical concentration. The fate of radical $HCO\cdot$ has been thoroughly discussed elsewhere (9).

Formation of Water, Hydrogen Peroxide, and Hydrogen

The formation reactions are believed to be:

$$H^{\cdot} + C_3H_8 \longrightarrow H_2 + C_3H_7^{\cdot} \quad (18)$$

$$OH^{\cdot} + C_3H_8 \longrightarrow H_2O + C_3H_7^{\cdot} \quad (19)$$

$$HO_2^{\cdot} + C_3H_8 \longrightarrow H_2O_2 + C_3H_7^{\cdot} \quad (20)$$

The hydrogen peroxide which is formed may decompose or react further. Hydrogen peroxide vapor is known to decompose heterogeneously at high temperatures to form water and oxygen even on relatively highly inert surfaces such as glass. Here it may also decompose homogeneously or react further with the other products of the oxidation.

The highest yield of hydrogen peroxide was 0.27 moles per mole of propane reacting at 425°C. Coating the surface with alkali halides or boric anhydride decreased the yield. The addition of propylene to the reaction mixture led to decreased amounts of hydrogen peroxide found per mole of oxygen reacted and this is shown in Figure 10. However this propylene addition did not greatly affect the yield of water plus hydrogen peroxide. Propylene may possibly be adsorbed on the surfaces of the reactor rendering them more active in decomposing hydrogen peroxide to water.

Heterogeneous Effects

Previous studies of hydrocarbon oxidation in glass vessels have shown that the results may vary as the reactor surface "ages". Such an aging process was very slow and relatively insignificant here. However, it is interesting to compare the present results with earlier results (17) which were obtained in the same laboratory under the same conditions and in the same type of reactor. After several hundred hours of operation, a brownish-red film was found deposited throughout the propane preheater and the internal surface of the lower section of the reactor used for the previous studies. Some film may also have been present throughout the remainder of the reactor, although it was not visible to the eye. The film dissolved in nitric acid and was combustible in oxygen. Presumably it was a polymeric substance resulting from polymerization of propylene and possibly also ethylene. The previous rate-of-reaction results are compared to the present ones in Figures 4 and 6 and it is seen that the induction period in the present studies was much shorter.

Figure 10 shows that the hydrogen peroxide yield per mole of propane reacted obtained in the previous studies was also much smaller than that obtained in the present work. It may be concluded that the propylene polymer forms a more active surface for the destruction of free radicals and hydrogen peroxide. Cleaning the previous reactor with nitric acid caused an increase in the reaction rate, an increase in the hydrogen peroxide yield, and also an increase in the ratio of acetaldehyde to formaldehyde in the products, the total aldehyde remaining essentially constant. This latter result suggests that at least some of the reactions of acetaldehyde leading to formaldehyde are heterogeneous in nature.

SUMMARY

The role of propylene in the partial oxidation of propane is seen to derive primarily from the relatively weak carbon-hydrogen bond compared to most other organic molecules. However, once the initial hydrogen has been removed from propylene, a relatively stable allyl radical results. This accounts for the acceleration effect of propylene in the initial stages of the propane oxidation, as well as its inhibiting effect under most other conditions.

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